

## Physical Properties of CdS/ITO Thin Films Growth by CBD Technique with Substrate Oscillating Agitation

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Cadmium sulphide (CdS) thin films deposited on indium tin oxide (ITO) substrates were prepared by chemical bath deposition technique by using different conditions to agitate the bath and the substrate. For substrate, an oscillating device working at 37 Hz was adapted to support each ITO substrate in order to agitate the substrate during deposition, meanwhile the chemical solution is heated and/not agitated. The deposited films were characterized on their morphology, on the band gap energy, and on thickness. The implemented novel technique for substrate oscillation has shown to improve the films quality, by the chemical bath without colloidal precipitates and by the clean film surfaces obtained. CdS films with variable deposition time can be achieved depending on the agitating technique. The mean band gap energy obtained around 2.41 eV is similar to the typical value reported in the literature for this material. In addition, by oscillating only the substrate during deposition is possible to obtain clean films and avoid the formation of colloidal precipitates on the chemical bath, normally presented when it is magnetically or ultrasonically agitated.

Keywords: Cadmium sulphide; Chemical bath deposition; Oscillating agitation

### I. INTRODUCTION

Cadmium sulphide (CdS) is a semiconductor material used as optical window joined with the active cadmium telluride (CdTe) semiconductor for thin film solar cells fabrication [1]. The chemical bath deposition (CBD) technique used to prepare CdS films, normally requires agitation to uniform the chemical bath since the formation of colloids and precipitates affect the film surface quality joined with the composition and the temperature of the chemical bath.

It is known that the physical properties of the CdS films depend on the deposition conditions, being the film surface flatness an important characteristic due to the scarce of formed hillocks. CdS/CdTe solar cells require a high quality interface in order to achieve good efficiencies. Chemical bath deposition is a low cost technique to prepare thin CdS films on glass or indium tin oxide (ITO) substrates [2]. Several works related with the deposition procedure have been published in the literature trying to obtain smoothing and surfaces free of hillocks to assure a good junction of the CdS when the CdTe layer is deposited [3].

Different works mention the importance of the chemical bath agitation, arguing better films quality. A great variety of agitation techniques for the chemical bath have been reported in the literature, being the magnetic stirrer the most common technique. Ultrasonic waves and microwaves techniques have been recently reported [4, 5] to improve the films quality when they are applied to agitate the chemical bath. However, substrate agitation is rarely reported during CdS deposition. In this work, we study the properties of CdS films deposited on ITO substrate agitated by means of an electric tooth-brush (oscillating device) and their comparison under different conditions of agitation.

### II. THEORY

The band gap energy value of the semiconductor films plays a key role on the solar cell functionality. The active semiconductor CdTe with a band gap of 1.5 eV has the most desirable value such that take advantage of the most important energetic solar spectrum in the visible range. Additional function has the CdS film which typically posses a band gap energy of 2.42 eV (515 nm) which acts as an optical window to improve the efficiency of the solar cell by reducing the spectrum range that can damage it. Given that CdS is a transparent film and presents a direct band gap ( $E_g$ ), we can measure this value by means of their transmittance (i.e. reflectance). By measuring the perpendicular transmittance and reflectance of the film, we can use the common relation to determine the  $E_g$  of the CdS films:

$$\alpha^2 = A(h\nu - E_g) \quad (1)$$

being  $\alpha$  the absorption coefficient,  $A$  is a constant, and  $h\nu$  the incident light energy (being  $h$  the Planck's constant and  $\nu$  the light frequency). For simplicity, we will use the common and widely used relation given in equation (1) for  $E_g$  calculations. A more complex relation can be used in order to reduce disturbance from the optical interference effect [6]. An error of 5% in the  $E_g$  reported values can be found when we use equation (1). According with equation (1), plotting  $(\alpha/h\nu)^{1/2}$  vs.  $h\nu$ , the band gap energy of the CdS film is given by the intersection point on the x-axis of the slope of the absorption coefficient. For  $E_g$  determination, the absorption coefficient of the ITO substrate was also taken into account, such that only  $E_g$  values for CdS films are reported.

### III. EXPERIMENTAL

CdS thin films were chemically deposited on  $1 \times 1 \text{ cm}^2$  ITO/glass substrates ( $R_{sITO} = 10 \pm 2 \ \Omega$ , 200 nm thickness,  $\rho_{ITO} = 2.53 \times 10^{-6} \ \Omega\text{-m}$  and  $E_{gITO} = 3.6 \text{ eV}$ ).

A typical chemical bath concentration reported in the literature formed by 0.02 M cadmium chloride (80 ml), 1.5 M ammonium nitrate (80 ml), 0.5 M potassium hydroxide (200 ml), and 0.2 M thiourea (80 ml) at  $348 \pm 2 \text{ K}$  of temperature was used in all chemical baths. A total volume of 440 ml of the chemical bath was formed after mixing the different components in the mentioned order. Thiourea is the last chemical component mixed into the bath such that the CdS formation starts when this component is included. ITO substrates were cleaned with soap, trichloroethylene, acetone and isopropyl alcohol according with a standard method rinsing with distilled water between each stage. Each clean ITO substrate is hold by a sample holder through an electrical tooth-brush (oscillating device). Oscillating device was characterized with a stroboscopic light and were found to oscillate at 45 Hz (free) and 37 Hz (immersed in the bath) as mean values. A Teflon home-made sample holder was designed for the ITO substrate which was adapted to the oscillating device for substrate oscillation. Five ITO substrates are immersed into the chemical bath and heated at 348 K, the deposition temperature. The chemical bath is heated (and stirred) with a heater-stirrer plate and its temperature measured with an Hg-thermometer immersed into the chemical bath. After the deposition temperature is reached, the thiourea is added and the CdS formation starts. Films are retired from the chemical bath one by one after 10, 20, 30, 40 and 50 min as deposition time and rinsed immediately with distilled water into an ultrasonic cleaner. We obtained pale-yellow films with CdS deposited on both substrate faces. The intensity of the color is related with the film thickness having minor intensity the thinnest films. After deposition, we obtained images of the surface morphology with the Atomic Force Microscopy (AFM) technique. After that, the CdS film deposited on the glass side is eliminated by means of a 10 % HCl solution. Thus, the  $E_g$  value is measured with the StellarNet APP2000 spectrophotometer adapted for transparent solids [7]. The band gap energy was computed from spectral data (transmittance and reflectance) obtained in the ultraviolet-visible range (from 200 to 850 nm of wavelength). Film thickness was measured with a Dektak 8 profilometer after forming a step in a film-corner with the HCl solution. In order to study the effects of the different agitation techniques, three different deposition conditions were used for CdS films preparation: a) substrate oscillation + magnetic agitation, b) only substrate oscillation, and c) without agitation.

### IV. RESULTS

Typical surface morphologies of CdS films from each deposition condition are shown in Fig. 1 as obtained by AFM technique. Several images of  $1 \times 1 \ \mu\text{m}^2$  size were obtained for each deposition time. The rms-roughness value was obtained from each image in order to analyze the surface quality. Following,

we will discuss the results of the three conditions studied.

#### a) Substrate oscillation + magnetic agitation.

For the first deposition condition, we combined the substrate oscillations produced by the oscillating device and the magnetic agitation of the bath produced with a teflon-covered magnetic stirrer. We deposited five CdS films with different deposition time. Fig. 2 shows the results obtained for the band gap energy and the film thickness parameters as a function of the deposition time. From Fig. 2a, the first two CdS films (10 and 20 min) presented larger values of  $E_g$  as compared with the typical value reported, a normal behaviour due to the minor thickness measured [8]. After that, next three CdS films presented typical band gap values between 2.41 and 2.42 eV. Fig. 2b, show the film thickness with time were a constant deposition rate (9 nm/min) during 30 min is observed. After this time, the chemical bath exhausted due to the constant film thickness. Rms-roughness on films was observed almost constant with time at 12 nm, except for the thinnest film which value was about 9 nm. Grain size was estimated from the AFM images and was found to be  $0.11 \ \mu\text{m}$  as a mean value with a slight increase with deposition time. For this condition, after films deposition, the chemical bath was cloudy and colloids and particles were observed at bottom, i.e., several chemical compounds precipitate along deposition.

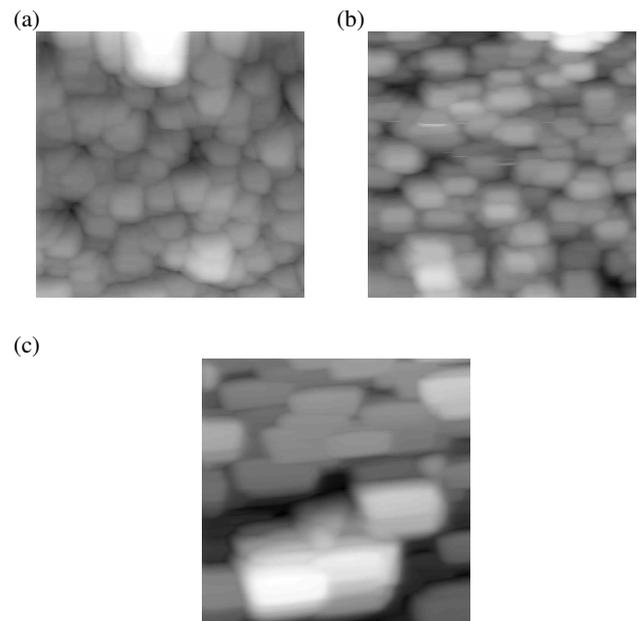


FIG. 1: AFM images ( $1 \times 1 \ \mu\text{m}^2$ ) of the CdS films deposited during 50 minutes by applying: (a) substrate oscillation + magnetic agitation, b) only substrate oscillation, and c) without any kind of agitation to the chemical bath.

#### b) Only substrate oscillation

Under this condition, the ITO substrates were maintained oscillating during CdS deposition. The chemical bath was

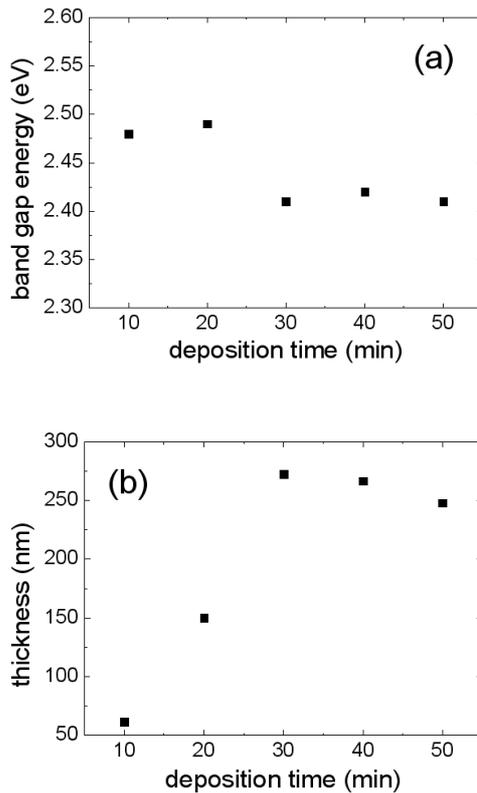


FIG. 2: Properties of the CdS films deposited with substrate oscillation + magnetic agitation: (a) band gap energy and (b) film thickness obtained as a function of deposition time.

magnetically agitated only to uniform the chemical components. Once the thiourea was added and the bath temperature was reached, the magnetic agitation is turned off and only the oscillating device remains working during films deposition. Fig. 3 shows the obtained results. The  $E_g$  values measured on films (Fig. 3a) were ranged between 2.40 and 2.45 eV, typical values on these films; however, an interesting difference was found on the rate deposition as compared with the before condition: a minor and a constant increasing on the rate deposition was observed with time (Fig. 3b).

Assuming a lineal behavior with time, we estimated the rate deposition as 6 nm/min. An amazing result was the clear and transparent chemical bath obtained after deposition (Fig. 4). Apparently, there were not colloidal particles or precipitates into the bath. Thus, the deposited CdS films show a clean surface, a desirable surface to receive the partner film. In order to be sure that the chemical bath is exhausted, we immersed a sixth substrate after 50 min of deposition time and retired 20 min after, but no more CdS deposition was observed. Thus, by using only substrate oscillation, the chemical bath exhausted after 50 min and the rate deposition decreases, producing clean films with good surface quality. Rms-roughness and grain sizes values measured on films were found similar than the obtained for the first condition.

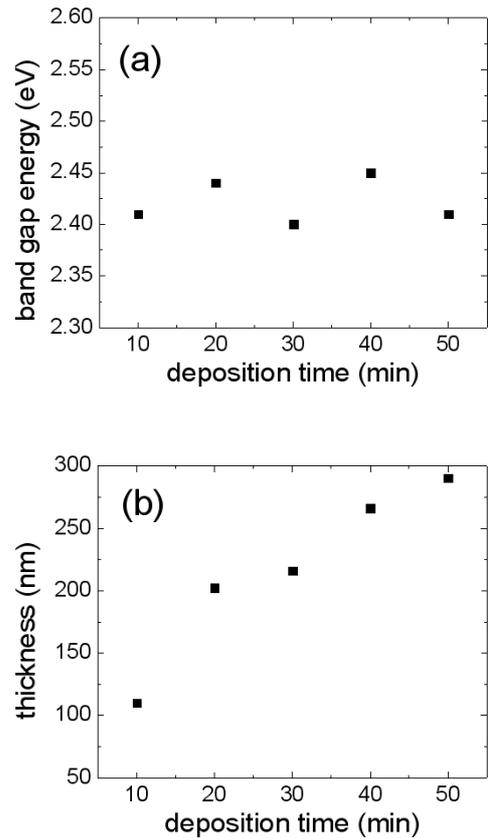


FIG. 3: Properties of the CdS films deposited with only substrate oscillation: (a) band gap energy, (b) film thickness obtained as a function of deposition time.

c) Without any oscillation We deposited CdS films with both the substrate and chemical bath without agitation. Only during the chemical bath formation, the magnetic agitation was used to uniform the concentration of chemical components. Results are shown in Fig. 5.



FIG. 4: Details of the oscillating device (tooth-brush), the sample-holder and the chemical bath. Clean CdS films and transparent chemical bath was obtained after deposition with this device.

The  $E_g$  values of the deposited films oscillate between 2.38 and 2.42 eV with a maximum value at 30 min (Fig. 5a); however, the film thickness reach a 180 nm value during the first 10 minutes of deposition, giving a mean rate of 18 nm/min

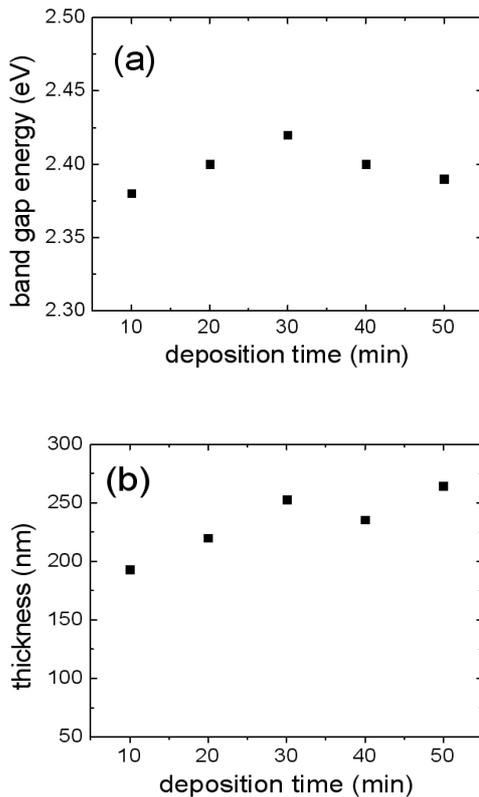


FIG. 5: Properties of the CdS films deposited without oscillation: (a) band gap energy, (b) film thickness obtained as a function of deposition time.

since the first deposited film. After this time, the deposition rate decreased at 2 nm/min for the next 40 minutes (Fig. 5b).

The resulted rms-roughness value was about 22 nm, larger than for the before conditions. After deposition, the chemical bath was cloudy with colloidal precipitates, producing dirty film surfaces. Here, the absence of agitation produced a higher rate deposition during first 10 min, after that, film thickness increases slowly. In all cases, the final film thickness reaches around 280 nm by the similar chemical concentration and bath temperature used.

## V. CONCLUSION

The effect of the ITO substrate agitation on the CdS films deposited by chemical bath was studied and compared under three different deposition conditions: substrate oscillation+magnetic agitation, only substrate oscillation, and without agitation.

A new mode to agitate the substrates by means of an oscillating device for CBD-CdS films deposition was proposed. Surface morphology, band gap energy, film thickness and rate deposition were obtained and discussed as a function of the different deposition condition. From our main results, by oscillating only the substrate at 37 Hz we obtained CdS films with a slow and constant rate deposition. Moreover, the chemical bath does not present colloidal precipitates after deposition, producing clean CdS films. Agitating the substrate and the chemical bath, the rate deposition increases and colloids and precipitates in the chemical bath are produced.

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